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## Phase Stability of Single Crystalline Co-Ni-Ga Shape Memory Alloy

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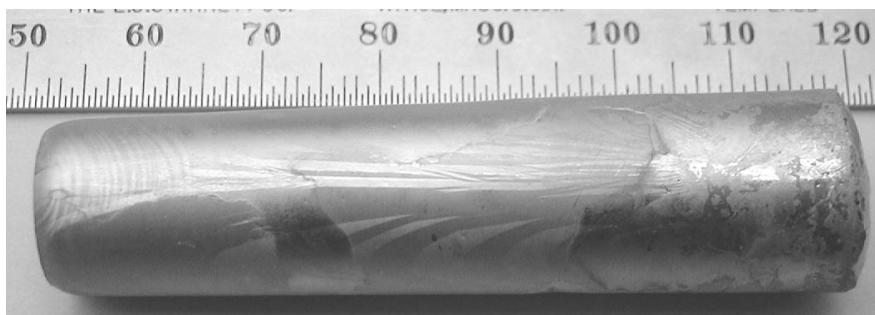
### ABSTRACT

Single crystals of  $\text{Co}_{48}\text{Ni}_{22}\text{Ga}_{30}$  have been synthesized using a modified Bridgman method. The ability to solidify and retain single phase B2 austenite was found to depend not only on the starting composition and growth rate, but also the ability to maintain sufficiently high cooling rates to avoid the precipitation of a Co-rich FCC phase during post-solidification cooling. DSC measurements on the single crystal found the  $M_s$ ,  $M_f$ ,  $A_s$ , and  $A_f$  to be 35.7°C, -1.8°C, 34.1°C and 72.2°C, respectively. On subsequent heating the B2 phase was found to partially decompose into the Co-rich phase at temperatures exceeding 380°C. Decomposition of the single phase B2 phase was tracked by microstructural observation, DSC, powder diffraction and low temperature heat capacity measurement. Restoration of the crystal to single phase B2 austenite required annealing of the crystal at temperatures above 1125°C followed by rapid cooling.

### INTRODUCTION

The recent investigations of shape memory transformations in Co-Ni-Ga alloys [1-4] have reported shape memory behavior comparable to those associated with other ternary Heusler alloys such as  $\text{Ni}_2\text{MnGa}$ . Initial measurements on Co-Ni-Ga alloys show similar trends to  $\text{Ni}_2\text{MnGa}$  alloys in both their dependence of martensitic transformation temperatures on electron concentration and saturation magnetization [2, 5]. However, unlike  $\text{Ni}_2\text{MnGa}$  alloys which are single phase over a large compositional range [6], recent phase equilibria investigations [3,4] have reported that  $\text{Co}_2\text{NiGa}$  alloys with transformations near room temperature lie within a two-phase field, similar to the Co-Ni-Al alloys [4,7,8]. This major difference in phase equilibria imposes significant limitations on the synthesis of single crystals as well as subsequent annealing and training of the martensitic transformation.

Studies of the solidification microstructures coupled with differential thermal analysis of Co-Ni-Ga alloys have shown these alloys solidify via a peritectic reaction, resulting in two phase mixtures of a Co-rich FCC phase and an austenitic B2 ordered phase. Our results agree with Oikawa et. al. [4]. In our study we concluded that the primary formation of FCC phase can be avoided by increasing the Ga content; however, the martensitic transformation is either suppressed to temperatures far below room temperature or eliminated completely due to the lowering of the electron concentration. The synthesis of single crystals of Co-Ni-Ga alloys therefore requires balancing the gallium content of the alloy to avoid solidification of a second phase during growth while maintaining the electron concentration sufficiently high for near room temperature martensitic transformations. Such a balance has been found for the composition  $\text{Co}_{48}\text{Ni}_{22}\text{Ga}_{30}$  as shown in Figure 1.



**Figure 1.** Single crystal of  $\text{Co}_{48}\text{Ni}_{22}\text{Ga}_{30}$  prepared by the Bridgman technique. Note the appearance of martensite twin boundaries on the surface indicating the transformation is above room temperature.

In this paper we report on the phase decomposition of single phase, single crystalline Co-Ni-Ga alloys when subjected to thermal annealing. Shape memory materials are often subjected to annealing to achieve a high degree of chemical order and to train the shape memory behavior; however, during annealing of the austenite phase in  $\text{Co}_{48}\text{Ni}_{22}\text{Ga}_{30}$ , a partial decomposition into a two phase mixture was found [4]. Precipitation of the second phase alters the composition of the austenite sufficiently to suppress the martensitic transition to temperatures well below room temperature. In this work, the decomposition of the austenite phase was tracked by microstructural observation, differential scanning calorimetry (DSC), and low temperature heat capacity measurements.

## EXPERIMENTAL

Appropriate quantities of cobalt (99.99 wt %), nickel (99.99 wt %) and gallium (99.999 wt %) were cleaned and arc melted several times under an argon atmosphere. The buttons were drop cast into a copper chill cast mold to ensure compositional homogeneity throughout the ingot. Crystal growth was done by the Bridgman technique in a resistance furnace. The as-cast ingot was placed in an alumina crucible and initially heated to  $900^{\circ}\text{C}$  under a vacuum of  $1.3 \times 10^{-4}$  Pa and then the furnace was backfilled with ultra high purity argon (99.99+%) to a pressure of  $2.8 \times 10^5$  Pa to minimize evaporative losses. Following pressurization, heating was continued until the ingot reached a temperature of  $1400^{\circ}\text{C}$ , held for 1 hour before being withdrawn at a rate of 20 mm/hr. Differential scanning and semi-adiabatic pulse calorimeters were used to characterize the shape memory transformation of the as-grown crystal.

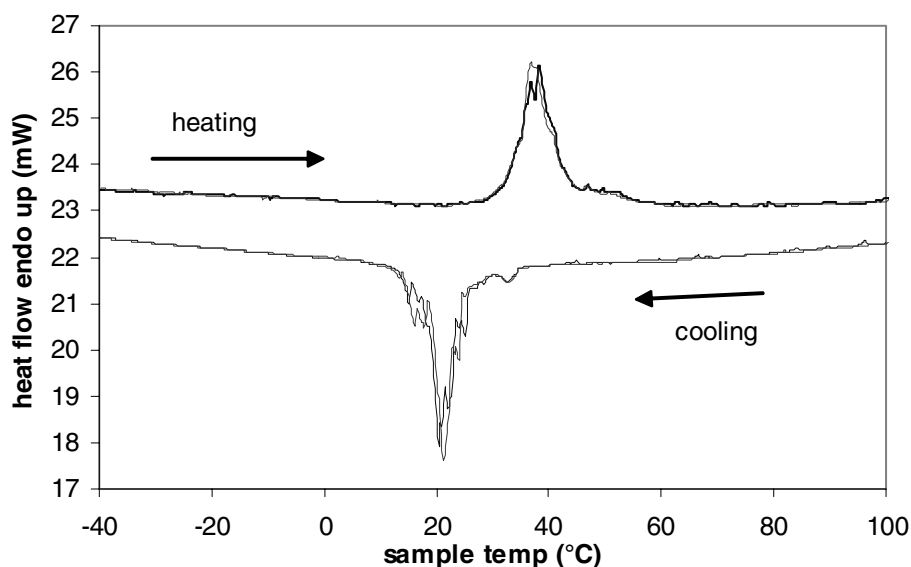
The occurrence of the decomposition of the austenite at elevated temperatures was observed in both continuous heating experiments using Perkin-Elmer TA7 DSC and high temperature x-ray diffraction as a function of temperature, and after isothermal anneals at various temperatures (see Table 1). The DSC was done on a thin slice of the as-grown crystal and powder made from another piece of the as-grown crystal was used for the high temperature x-ray diffraction experiment. Isothermal annealing of samples cut from the as-grown ingot was done under controlled atmosphere and either slow cooled at a rate of  $10^{\circ}\text{C}/\text{min}$  or quenched into either water or oil. (See Table 1). The annealed samples were polished using standard metallographic techniques and characterized using a Hitachi scanning electron microscopy (SEM) in conjunction with energy dispersive spectroscopy (EDS).

**Table 1.** Isothermal annealing conditions and results of microstructural evaluation of annealed single crystal  $\text{Co}_{48}\text{Ni}_{22}\text{Ga}_{30}$ . Compositions determined by energy dispersive spectroscopy.

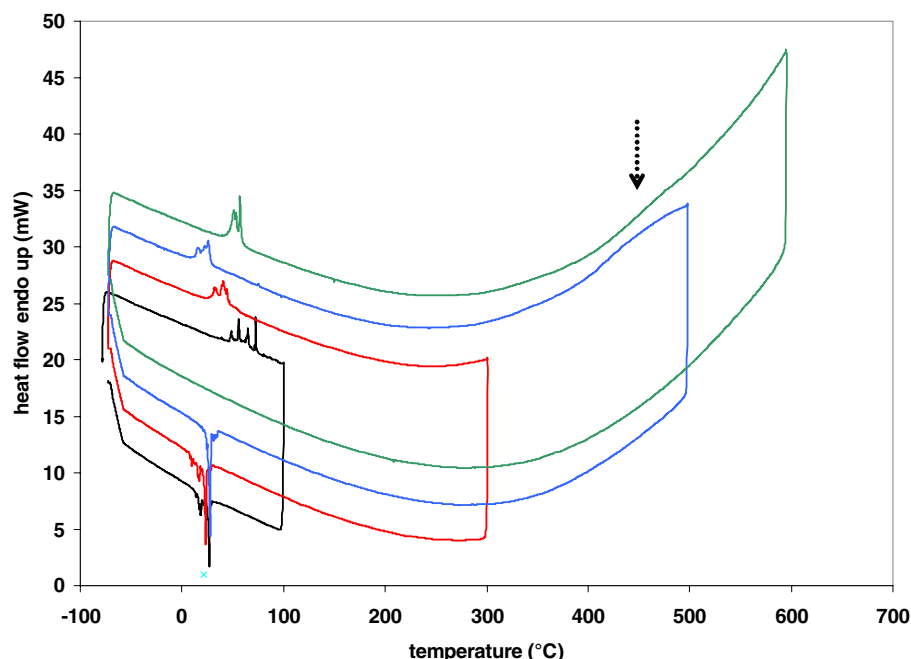
anneal temp, °C	duration (hrs)	cooling method	matrix composition at%	2nd phase composition at%
---	---	as grown	$\text{Co}_{47.8}\text{Ni}_{21.9}\text{Ga}_{30.3}$	Single phase matrix
300	24	slow cool	$\text{Co}_{48}\text{Ni}_{21}\text{Ga}_{31}$	Single phase matrix
500	24	slow cool	$\text{Co}_{48}\text{Ni}_{21}\text{Ga}_{31}$	Present(too small to analyze)
900	24	slow cool	$\text{Co}_{45.8}\text{Ni}_{22.7}\text{Ga}_{31.5}$	$\text{Co}_{61.7}\text{Ni}_{18.5}\text{Ga}_{19.8}$
900	24	water quench	$\text{Co}_{46.8}\text{Ni}_{22.5}\text{Ga}_{30.7}$	$\text{Co}_{63.3}\text{Ni}_{17.2}\text{Ga}_{19.5}$
1050	24	water quench	$\text{Co}_{45.6}\text{Ni}_{21.8}\text{Ga}_{32.7}$	$\text{Co}_{60.9}\text{Ni}_{17.9}\text{Ga}_{21.2}$
1125	1	oil quench	$\text{Co}_{48.3}\text{Ni}_{22.1}\text{Ga}_{29.7}$	Single phase matrix

## RESULTS

Microstructural examination of the as-grown crystal showed no evidence of second phase precipitation following solidification. Composition of the single phase matrix, as determined by EDS, was close to the nominal  $\text{Co}_{48}\text{Ni}_{22}\text{Ga}_{30}$ . The martensite and austenite transformation temperatures,  $M_s$ ,  $M_f$ ,  $A_s$ , and  $A_f$ , 35.7°C, -1.8°C, 34.1°C and 72.2°C, respectively, were determined by DSC heating and cooling traces as shown in Figure 2. Powder XRD analysis as a function of temperature indicates the structure of the martensitic phase is orthorhombic and the high temperature phase is B2 CsCl, as expected [2].



**Figure 2.** Differential scanning calorimetry traces of heating and cooling cycles of the as-grown  $\text{Co}_{48}\text{Ni}_{22}\text{Ga}_{30}$ . Heating and cooling rates are 10 °C/min.



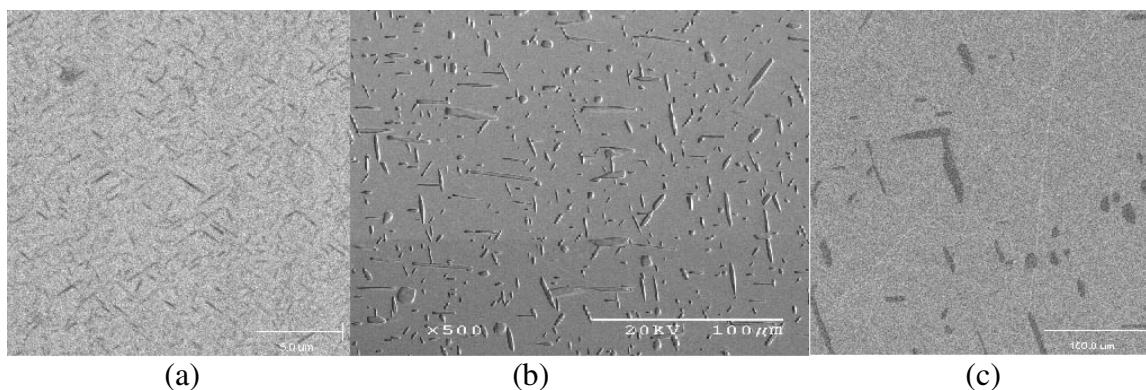
**Figure 3.** Decomposition of the single phase matrix tracked by continuous cycling at increasing temperatures in the DSC. Arrow indicates the broad peak associated with precipitation of second phase. Note, following the 600°C cycle, the martensite transformation has been eliminated.

### Decomposition during continuous heating

The decomposition of the single phase  $\text{Co}_{48}\text{Ni}_{22}\text{Ga}_{30}$  and its effect on the martensite-austenite transformations can be easily observed by repeatedly cycling a single sample in the DSC while progressively raising the maximum temperature on each cycle as is shown in Figure 3. The decomposition was found to begin around 380°C and end around 540°C where a shallow and broad heat release associated with the precipitation of the second phase, is observed (as indicated by the arrow in Figure 3) most notably in the 500 °C trace and to a lesser extent in the 600 °C trace. Despite evidence of precipitation at temperatures below 500°C, the martensite transformation appears to be relatively unaffected. The martensite peak on cooling does not shift in temperature following each cycle. In contrast, the reverse austenite transformation generally shifts to lower temperatures as the maximum temperature is increased. Once the sample had been cycled to 600°C the martensite transformation was completely absent in the subsequent cooling cycle. Additional DSC runs shows that the elimination of the transformation following the 600°C treatment was irreversible.

### Isothermal decomposition

Oriented samples of the as-grown crystal were annealed at 300°C, 500°C, 900°C, 1050°C and 1125°C for a minimum of 1 hr followed by slow cooling at 10°C/min or quenching, see Table 1. Some samples were slow cooled rather than quenched to mimic conditions during a typical crystal growth. The samples annealed at 300°C and 1125°C were single phase after being annealed. However, the martensite lines in the sample annealed at 300°C were reduced in

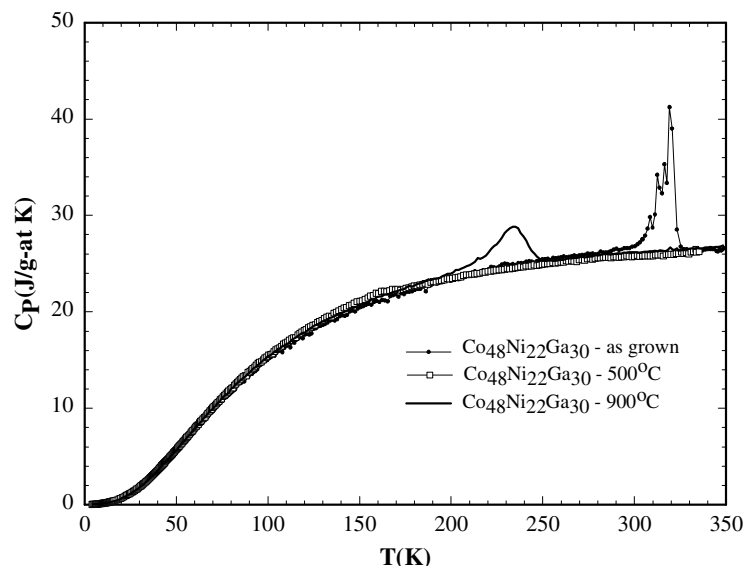


**Figure 4.** Micrographs of single crystal samples heat treated for 24 hours at various temperatures. (a) 500°C and slow cooled. (b) 900°C and water quenched. (c) 1050°C and water quenched. Compositions of the phases can be found in Table 1.

size compared to an as-grown sample, and only occurred along edges of the sample. The remaining samples show an increase in the size of second phase present as the annealing temperature increases as shown in Figure 4. Compositional analyses of the precipitates indicate an enriched Co content consistent with the FCC Co-rich terminal phase identified by Oikawa et. al. [4]. There is also a corresponding decrease in the Co-content of the matrix composition that suggests, based on the reduction of electron concentration [2]; the martensite transformation should be suppressed to lower compositions. Indeed the room temperature microstructures show no evidence of the martensitic formation for samples annealed at 500°C, 900°C and 1050°C, but surface relief associated with formation of martensite was visible after cooling in liquid nitrogen showing the  $M_s$  to be at or above  $-196^\circ\text{C}$ . This depression of the  $M_s$  temperature is clearly seen in low temperature heat capacity measurements shown in Figure 5. The transformation temperature has been reduced to  $-98^\circ\text{C}$  (175 K) (and almost eliminated) following the 500°C anneal and partially restored to  $-38^\circ\text{C}$  (235 K) following the 900°C anneal. Finally, the shape memory transformation was re-established to its original as-grown state by annealing at or above  $1125^\circ\text{C}$ .

## CONCLUSION

Single crystal samples of  $\text{Co}_{48}\text{Ni}_{22}\text{Ga}_{30}$  were found to precipitate a second phase during post-growth anneals, which by altering the composition of the matrix, shifts the shape memory transitions to well below room temperature as seen in heat capacity data. Thermal analysis shows the precipitation of the second phase begins at temperatures above  $380^\circ\text{C}$ . Additional studies involving isothermal annealing at various temperatures identified the precipitates as Co-rich FCC phase. The depletion of Co from the matrix phase lowers the electron concentration with a corresponding decrease in transition temperature. The degree to which the martensite transformation temperature was lowered depended on the annealing temperature with the greatest change at low temperatures. As the annealing temperature increased, the transition temperature also increased toward the original room temperature value, with complete restoration at an annealing temperature of  $1125^\circ\text{C}$ .



**Figure 5.** Low temperature heat capacity measurements showing the depression of the martensitic transformation to lower temperatures following isothermal annealing.

## ACKNOWLEDGEMENTS

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